Study on the gelation rate of at-polystyrene/CS_2 solutions*

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The gelation rate of atactic polystyrene in the solvent carbon disulphide has been studied. The time required to form a gel (gelation time) was measured as a function of gelation temperature, polymer concentration and molecular weight. A master curve was found for the gelation time–gelation temperature curves at various polymer concentrations by shifting the curves along the temperature axis. This means that a simple reduction between concentration and gelation temperature is possible for the rate of gelation, independently of the molecular weight of the polymer. It was also found that the temperature shift is attributable to the difference in the gel melting temperatures at different polymer concentrations, The critical gelation temperature was found to be ≈13°C lower than the gel melting temperature at a given polymer concentration. These results indicate that gelation in this system is a first-order transition and signify that the dependence of gelation rate on polymer concentration and molecular weight is related to their effects on the gel melting temperature T^g_m. The apparent activation energy of gelation at temperature T was found to be proportional to $(T^g_m - T)^{-2.8}$.

(Keywords: atactic polystyrene; carbon disulphide; thermoreversible physical gels; gelation time; gelation rate; gelation temperature; hysteresis; supercooling temperature; activation energy)

INTRODUCTION

Thermoreversible physical polymer gels are regarded as three-dimensional networks whose junction points consist of physical bonds[1,2]. However, the nature and structure of junction points are so complex that they still remain unsolved uniquely. The gelation of some crystalline homopolymers and copolymers has been analysed in the same way as for crystallization[3–13], since crystallization is considered to correspond to thermoreversible gelation, with a small number of exceptions such as gelatin–water[14] and poly(vinyl chloride)–dioxane[15] systems in which hydrogen bonds play an important role.

However, Wellinghoff *et al.* and Tan *et al.*[16–18] recently reported that non-crystallizable atactic polystyrene (at-Pst) makes thermoreversible gels from solutions of many different solvents. They demonstrated that entanglement of polymer chains in solution or phase separation following spinodal decomposition is not necessary for physical gelation of at-Pst. Furthermore, they and Boyer *et al.*[19] investigated at-Pst gels in detail as a function of molecular weight of polymer, polymer concentration in solution and species of solvent and proposed that gelation is caused by a second-order transition occurring at a characteristic temperature T_{11} which is higher than the glass transition point. Guenet and co-workers[20,21] demonstrated that enhanced low-angle light scattering (ELAS) was observed for at-Pst solutions even above the gel melting point T^g_m where three-dimensional gel networks vanish. They followed the gel formation with differential scanning calorimetry (d.s.c.)[22], and suggested that at-Pst solutions form polymer–solvent complexes or stoichiometric compounds. Berghmans *et al.*[23] investigated gelation of at-Pst/decalin and showed that gelation results from localized liquid–liquid phase separation on cooling followed by a vitrification process.

These reviews indicate that there is still much ambiguity in the gelation mechanism of at-Pst solutions. Recently, Mandelkern *et al.*[24] found that thermodynamic properties of the gels changed continuously from homopolymer to highly branched copolymer, e.g. the hydrogenated polybutadiene series and the ethylene–vinyl acetate copolymers. Melting temperatures determined by d.s.c. were the same as those determined by a ball drop method, which implied that crystallization is a necessary requirement for gelation. They also investigated the temperature dependence of gelation rate for these polymers, and found that their gelation time–temperature curves can be superimposed by shifting along the temperature axis. Consequently, it was concluded that the gelation mechanism is the same for all their samples of homopolymers and copolymers. It is supposed that gelation rate is influenced commonly by crystallization in the case of crystallizable homopolymers and copolymers, as in the poly(vinyl alcohol)–water system[25]. It is difficult to expect similar results for non-crystalline polymer.

In this paper, the gelation of a non-crystallizable at-Pst is investigated: the gelation rate of at-Pst/CS_2 solution is studied as a function of gelation temperature, polymer concentration of solution and molecular weight of polymers. The activation energy of the gelation process, estimated from the temperature dependence of the gelation rate, is discussed in relation to the gelation temperature.

EXPERIMENTAL

Materials and sample preparation

Two commercially available at-Pst polymers ($M_w = 28 \times 10^4$, $M_w/M_n = 2.5$ and $M_w = 218 \times 10^4$, $M_w/M_n = 1.3$)

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were used. CS$_2$ of high purity grade was used as solvent, after being dried over molecular sieves.

An appropriate amount of at-Pst and solvent were put into a glass tube with an inner diameter of 12 mm to be sealed. The polymer concentration varied from 150 g l^{-1} to 400 g l^{-1} and from 40 g l^{-1} to 100 g l^{-1} for samples of molecular weights 28×10^4 and 218×10^4, respectively. Although the polymer was dissolved almost instantly into solvent at room temperature, the solutions were kept standing for 3 d to improve homogenization.

Gelation time measurement

The solution in the tube was quenched in a bath containing ethanol–methanol mixtures kept at a fixed temperature, measured by a thermocouple and a thermoelectric thermometer. The gelation point, where the solution lost its fluidity, was determined by a tube tilting method. The gelation time was defined as the time from the instant when the tube was put in the bath at a fixed temperature to the gelation point. Before gelation experiments, cooling rates of the solutions in test tubes during quenching were checked at the various temperatures at which we expected to do the experiments. The results shown in *Figure 1* indicate some delay in cooling of solution: each fixed gelation temperature is reached in $\leqslant$200 s. It is difficult to compensate for the effect of delay of cooling on the gelation time. Note, however, that the fact that the higher the temperature, the lower was the gelation rate helped to decrease the experimental error due to the delay of cooling in this case. Note also that in this study our main interest was not in the data obtained at short gelation time.

Gel melting temperature measurement

After being kept standing at given temperatures for over one week, the test tubes were put upside down in a temperature controlled bath and then heated at a rate of about 3°C h^{-1}. The temperature at which the meniscus began to flow was defined as the gel melting temperature.

RESULTS AND DISCUSSION

The gelation time of CS$_2$ solutions of at-Pst with different molecular weights is shown in *Figure 2* as a function of gelation temperature and polymer concentration. The temperature dependence of gelation time is large at high temperatures but small at low temperatures. There is a limit of gelation temperature for each gelation above which the gelation time becomes infinite. The span of measurable gelation temperature is only ≈15°C for all the polymer concentrations studied. Note that all the gelation time–temperature curves observed at various polymer concentrations are essentially similar and that shifting the curves along the temperature axis results in a master curve as shown in *Figure 3*. This means that a simple reduction property exists between polymer concentration and gelation temperature for the two polymers with different molecular weights.

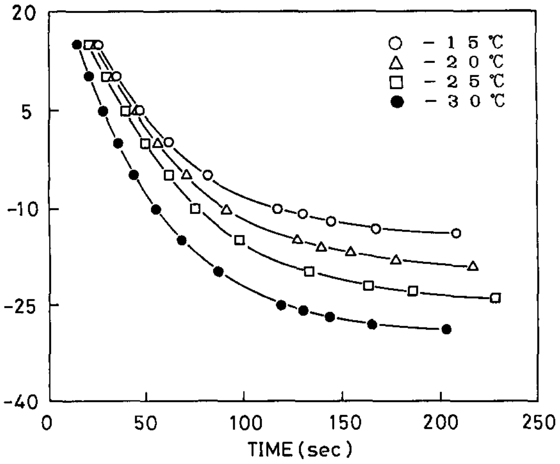

Figure 1 Cooling rate of an at-Pst/CS$_2$ solution at various temperatures

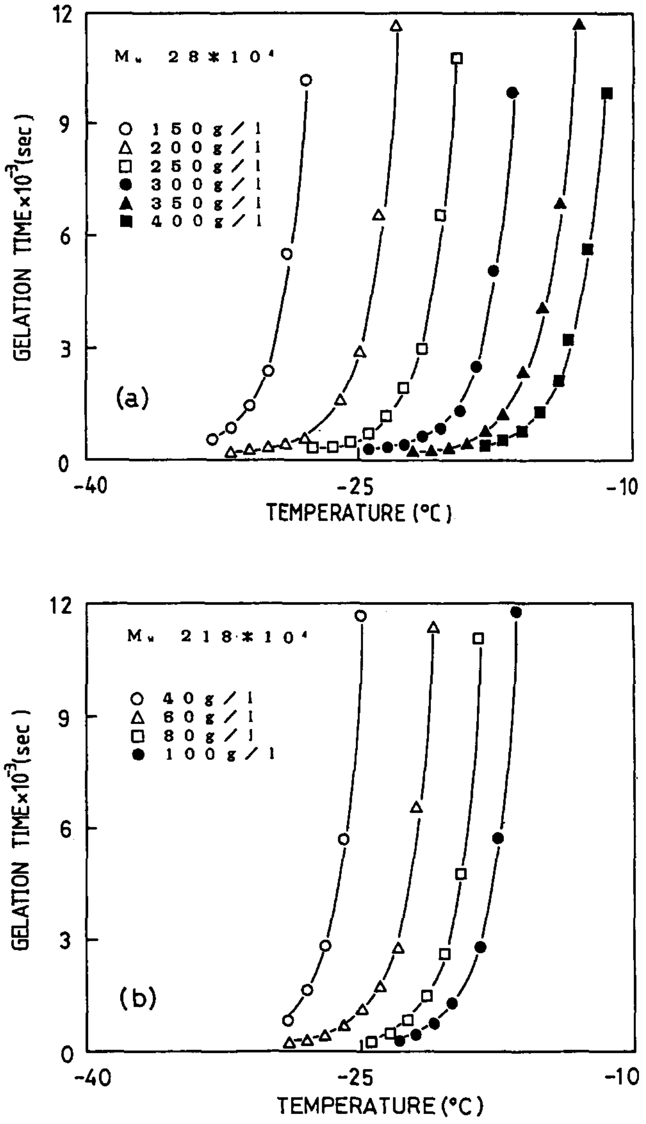

Figure 2 Plot of gelation time against gelation temperature for various at-Pst concentrations

This result is consistent with that for the gelation of crystalline polymers, reported by Mandelkern *et al.*[24]. The mechanisms of gelation are possibly different between the crystalline and amorphous polymers. Therefore, it is interesting that the same reduction property is observed for both non-crystalline at-Pst gels and crystalline polymer gels.

Figure 3 shows the composite gelation time–temperature curve obtained by shifting the curves in *Figure 2a* along the temperature axis to that for 150 g l^{-1}. *Figure 4* shows the shift temperature in making the composite curve as a function of polymer concentration. The shift

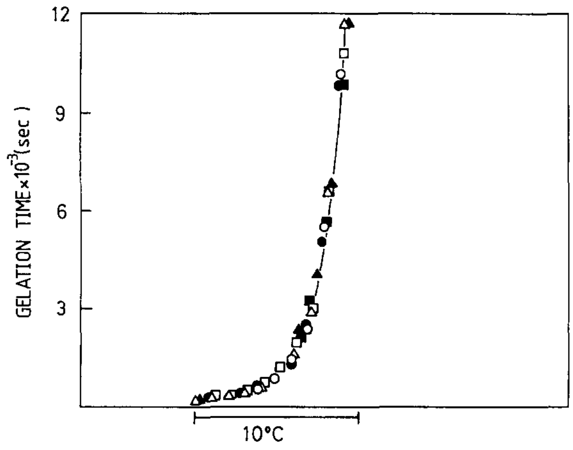

Figure 3 Gelation time–temperature curve obtained by superimposing curves of *Figure 2a*

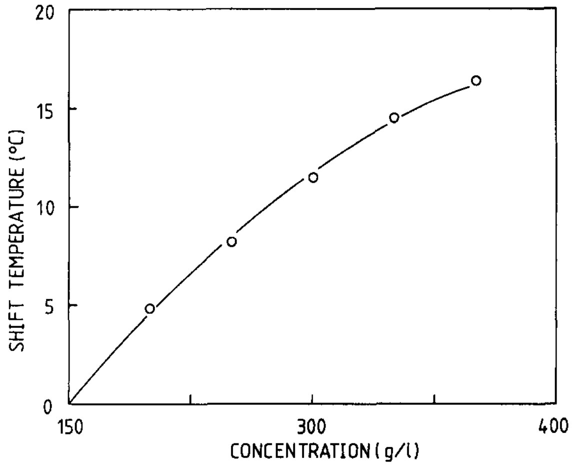

Figure 4 Shift temperature used in making superposition in *Figure 3* as a function of polymer concentration. The curve for 150 g l^{-1} is taken as the standard

temperature increases with increasing polymer concentration. The relation between polymer concentration and gelation temperature can be written as follows:

$$t_{gel}(C, T) = t_{gel}(C_0, T_0 + \Delta T) \qquad (1)$$

where $t_{gel}(C, T)$ is the gelation time at temperature T of a solution whose concentration is C, C_0 and T_0 are the concentration and gelation temperature for a solution which is arbitrarily chosen as standard, and ΔT is the shift temperature, which depends only on the concentration, as will be discussed in detail below.

Figure 2 shows that there is a critical gelation temperature above which no gelation takes place at a given polymer concentration. To obtain the relation between critical gelation temperature and polymer concentration, the data in *Figure 2* were replotted in *Figure 5*, where the gelation rate is defined as the reciprocal of gelation time. Each curve in *Figure 5* is for a fixed gelation temperature. Extrapolation of each curve to $1/t = 0$, i.e. gelation rate 0, gives the critical concentrations at these fixed temperatures. No solution below the critical concentration can form a gel at the given temperature. The data on critical concentration at given temperatures, on the other hand, give the critical temperature above which no gelation takes place at a given polymer concentration. Critical gelation temperatures thus obtained are plotted with solid symbols in *Figure 6*. The gel melting temperature measured on heating is shown for the two polymers as a function of polymer concentration by the open symbols in *Figure 6*. The figure indicates that sol–gel curves estimated from gelation are about 13°C lower than those estimated from gel melting. This hysteresis showed that the gelation has a rate process and seems to contradict the conclusion of Tan *et al.*[17] that gelation is an equilibrium process in which no hysteresis is expected. Since it has been clarified that the gelation of the at-Pst/CS$_2$ system is a first-order transition[22,26], the existence of hysteresis in this system is intrinsic.

The gelation rate is strongly dependent on the supercooling temperature, which is the difference between gel melting and gelation temperature, as shown in *Figure 7*. Note that in *Figure 7a* and *b* the rates increase with increasing supercooling temperature, irrespective of the polymer concentration and molecular weight. This simply shows that no gelation takes place, at any of the polymer concentrations studied, unless the supercooling temperature is >13°C.

The result of *Figure 7* also implies that the temperature shift in the reduction of gelation time to gelation temperature in *Figure 4* is related simply to the difference between the gel melting temperatures at different polymer concentrations. This is explicit in *Figure 8*, which shows

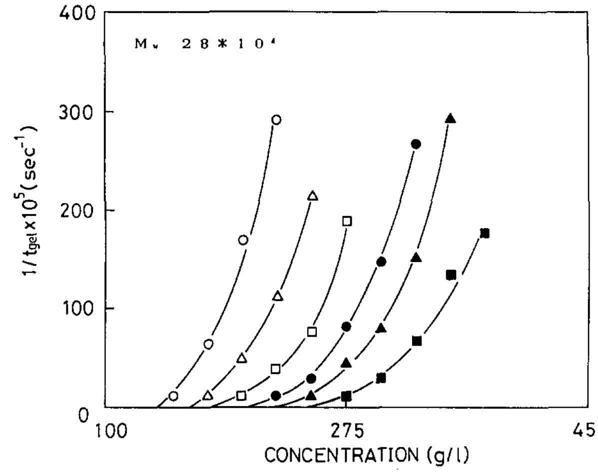

Figure 5 Plot of reciprocal gelation time (rate of gelation) against polymer concentration at various gelation temperatures (°C): ○, −28.1; △, −25.5; □, −23.3; ●, −21.4; ▲, −19.9; ■, −18.0

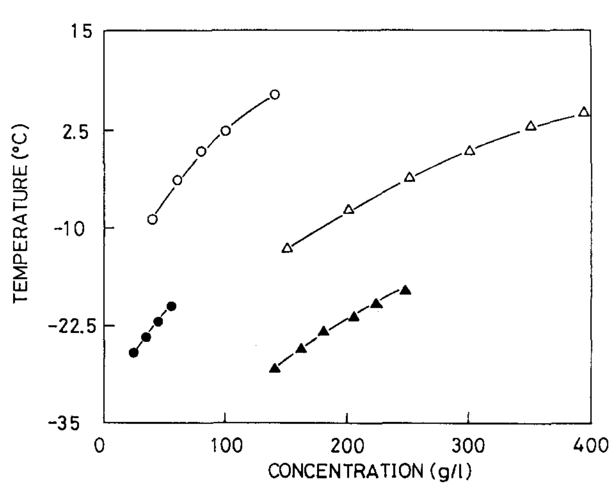

Figure 6 Comparison of gel melting temperature (○, △) and critical gelation temperature (●, ▲) obtained from *Figure 5* for two samples: ○, ●, $M_w = 218 \times 10^4$; △, ▲, $M_w = 28 \times 10^4$

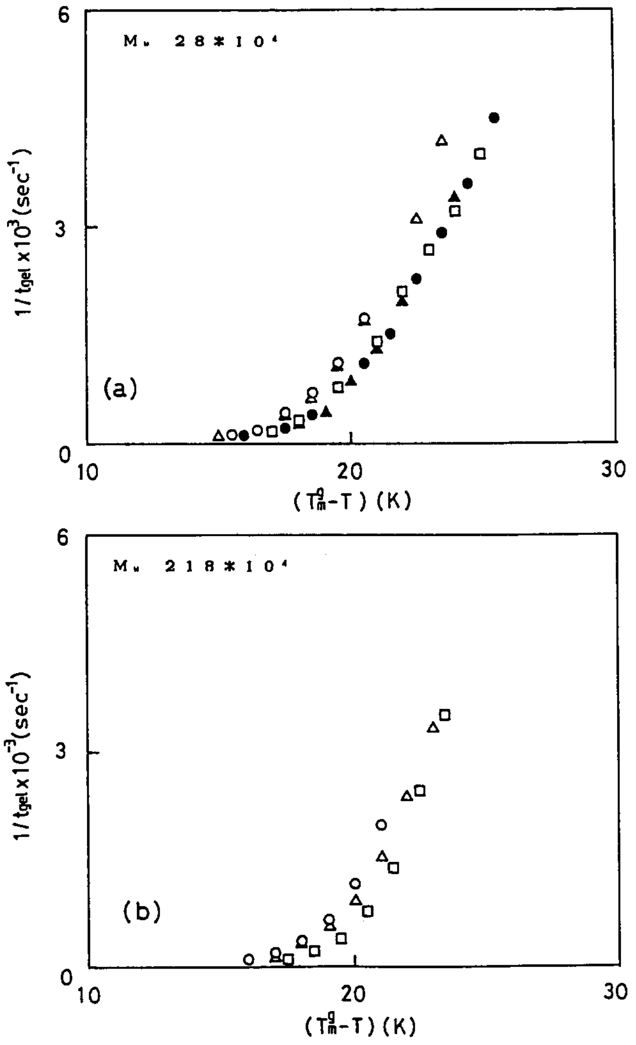

Figure 7 Dependence of reciprocal gelation time (rate of gelation) on supercooling temperature for various polymer concentrations (g l^{-1}): (a) ○, 150; △, 200; □, 250; ●, 300; ▲, 350; ■, 400; (b) ○, 40; △, 60; □, 80

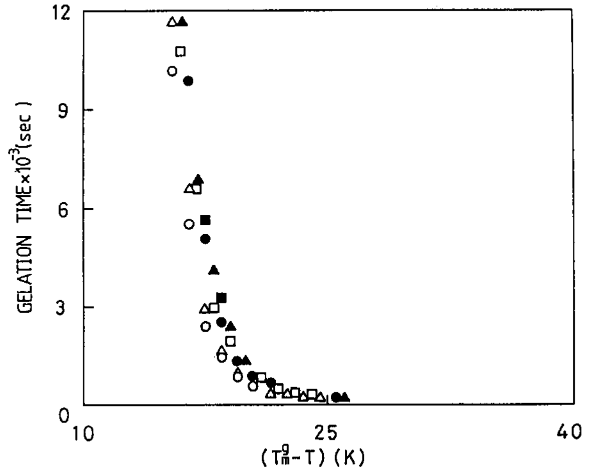

Figure 8 Gelation time against supercooling temperature for various polymer concentrations (g l^{-1}): ○, 150; △, 200; □, 250; ●, 300; ▲, 350; ■, 400. $M_w = 28 \times 10^4$

the relation between gelation time and supercooling temperature.

The results obtained above are important, for they show that all the effects of polymer concentration and molecular weight on the rate of gelation are related directly to their effects on the gel melting temperature.

The apparent activation energy in gelation ΔE^+ was calculated using an Arrhenius relation:

$$1/t_{\mathrm{gel}} \sim \exp(-\Delta E^+/RT) \qquad (2)$$

where t_{gel} is the gelation time, and therefore, $1/t_{\mathrm{gel}}$ is proportional to the rate of gelation. The logarithm of the gelation time at three polymer concentrations is plotted against reciprocal temperature in *Figure 9*. Although the plots are not straight lines, the tangent of a curve at a given temperature gives the activation energy at the gelation temperature. Activation energies of gelation thus obtained are plotted against supercooling temperature in *Figure 10*, indicating that the activation energy decreases exponentially with increasing supercooling temperature:

$$\Delta E^+ \sim (T_m^g - T)^{-2.8} \qquad (3)$$

where T_m^g is the melting point of a given gel. It is well known that the corresponding index is equal to -1 in crystallization due to two-dimensional nuclear growth, as in the case of polyethylene shown in *Table 1*. According to Ogasawara[25], in the gelation of polyvinyl alcohol aqueous solutions the index is equal to -2, indicating three-dimensional growth. It is currently difficult to explain the meaning of the index -2.8 in the gelation of at-Pst/CS$_2$ solutions.

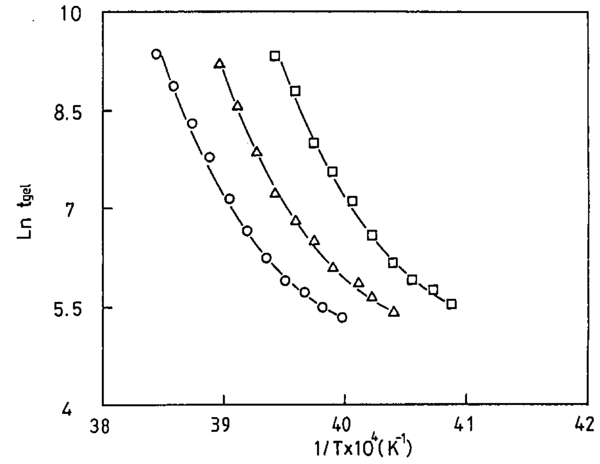

Figure 9 Arrhenius plot of logarithm of gelation time against reciprocal gelation temperature for various polymer concentrations (g l^{-1}): ○, 250; △, 300; □, 350

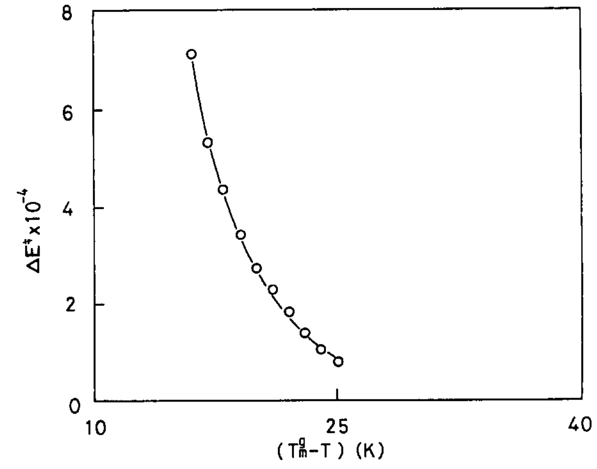

Figure 10 Dependence of activation energy of gelation on supercooling temperature

Table 1 Relation between growth rate and supercooling temperature in polymer crystallization and gelation

Polymer	Type	Related equation
PE in xylene[27]	Crystallization	$\sim\exp(1/T\,\Delta T)$
PVA in water[25]	Gelation	$\sim\exp(1/T\,\Delta T^2)$
At-Pst in CS$_2$[a]	Gelation	$\sim\exp(1/T\,\Delta T^{2.8})$

[a] This work

SUMMARY

Gelation rate at a given temperature varies with polymer concentration. However, gelation time–temperature curves at different polymer concentrations can be reduced to a master curve simply by shifting them along the temperature axis. This means that a simple reduction between polymer concentration and gelation temperature exists for the rate of gelation.

The gel melting point increases with increasing polymer concentration. The shift temperature in gelation time–temperature reduction is related to the gel melting point. Further, the effect of the degree of polymerization on the rate of gelation is also related to its effect on the gel melting point. The critical gelation temperature at a given polymer concentration is ≈13°C lower than the gel melting point.

The apparent activation energy of gelation, from an Arrhenius type equation, is proportional to $(T_m^g - T)^{-2.8}$, irrespective of the polymer concentration and the molecular weight. But the point made in the preceding paragraph indicates that $T_m^g - T$ must be >13°C in this case.

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